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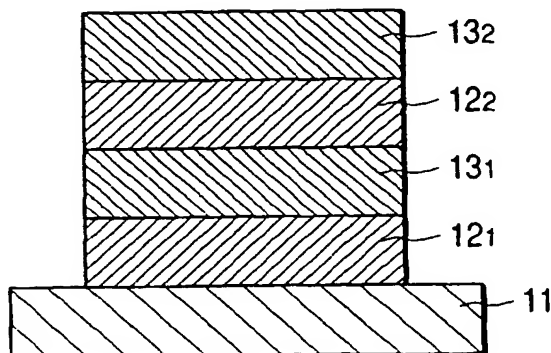
(54) Optical-thin-film material, process for its production, and optical device making use of the optical-thin-film material

(57) An optical-thin-film material comprising a metal oxide containing samarium and titanium, or comprising a compound represented by the following chemical formula:



wherein $-1 < x < 1$ is disclosed. An optical device having an optical thin film formed of such a material is also disclosed. This optical-thin-film material does not cause any compositional deviation to enable continuous deposition when used as a vacuum deposition material, and does not cause any deterioration due to ultraviolet-light irradiation.

FIG. 2



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Description

BACKGROUND OF THE INVENTION

5 Field of the Invention

[0001] This invention relates to an optical-thin-film material used to coat lenses, mirrors and prisms used in optical instruments such as cameras and video cameras or to coat optical devices such as optical disks. It also relates to an optical device provided with an optical thin film formed by coating such a material.

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Related Background Art

[0002] In cameras, video cameras and other optical instruments, metal oxide thin-film coating is utilized in their anti-reflection films, filters, mirrors and so forth in order to enhance or reduce the reflection of light or in order to absorb or transmit specific wavelength light.

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[0003] Of these metal oxide optical thin films, in particular, multi-layer thin films alternately superposingly formed of thin films having a high refractive index and thin films having a low refractive index can selectively transmit or reflect specific wavelength light. Hence, they are used as a coating material for optical filters or prisms in a large number in optical instruments as typified by projectors. Such multi-layer thin films are produced by physical vapor deposition (PVD) as typified by vacuum deposition (or evaporation) and sputtering. These multi-layer thin films, however, have so large a total number of films that it often takes a long time for film formation to have a problem a low productivity. As a counter-measure therefor, the designing of multi-layer thin films is elaborated to lessen the total number of films. As other measures, in vacuum deposition, films are formed at a high rate or materials are used which can enjoy a short premelt time for stabilizing evaporation sources. In sputtering, magnetron sputtering is employed, intending to form films at a higher rate. Also, in order to improve productivity, film-forming systems are being shifted from batch type systems to continuous type systems.

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[0004] In the case of the continuous type systems in vacuum deposition, films are formed while supplying substrates and replenishing evaporation source targets. Hence, the evaporation source targets must be those having shapes suited for individual systems and also can attain stable characteristics during continuous use. In general, when the multi-layer thin films alternately superposingly formed of high-refractive-index thin films and low-refractive-index thin films are formed, materials that may cause variations in refractive index because of compositional variations or materials that have much non-homogeneity are not preferable as evaporation substances when the multi-layer thin films are formed by the continuous type systems.

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[0005] When these filters and prisms coated with the coating material are used as beam splitters in optical instruments, optical multi-layer thin films are often face to face bonded with adhesives when used. As the adhesives, ultraviolet-curable resins are used in view of an advantage that they can cure in a short time and any solvent need not be used, where widely used is a method in which the ultraviolet-curable resins are irradiated by ultraviolet light to cure to join the thin films. However, such ultraviolet-light irradiation causes the metal oxide optical thin films to undergo deoxydation reaction due to photochemical reaction, bringing about a problem of a deterioration of optical thin films, e.g., a decrease in light transmission.

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[0006] As materials that may neither cause any compositional variations nor has any non-homogeneity and has a high refractive index, a compound represented by the formula: $\text{La}_2\text{Ti}_2\text{O}_{7-x}$ (wherein x is 0.3 to 0.7) is known in the art as disclosed in Japanese Patent Application Laid-Open No. 6-235803.

[0007] However, in deposition materials conventionally used for optical thin films having a high refractive index as stated above, the materials may so greatly scatter that it takes a long premelt time for stabilizing evaporation sources, or their continuous use may cause compositional changes, resulting in a change in refractive index. Also, because of a certain non-homogeneity, the multi-layer formation of films may result in a difference of values from designed values. Still also, the irradiation to deposited thin films with ultraviolet light may cause an increase in absorptivity to make it unable to bond the thin films by using the ultraviolet-curable resins. There are such various problems.

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[0008] In the compound represented by the formula $\text{La}_2\text{Ti}_2\text{O}_{7-x}$ ($x = 0.3$ to 0.7), too, although it is a material that may neither cause any compositional variations nor has any non-homogeneity and has a high refractive index, this material may so greatly scatter at the time of premelting that it must be premelted for a long time every time materials are added. Moreover, it may cause a deterioration due to irradiation with ultraviolet light. Thus, this material is not a preferred material.

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[0009] As materials for optical thin films, substances or compounds are required which have a refractive index intermediate between that of aluminum oxide (Al_2O_3), having a refractive index of about 1.65, and that of zirconium oxide (ZrO_2), having a refractive index of about 2.0. Such substances or compounds include silicon monoxide (SiO), magnesium oxide (MgO), lead fluoride (PbF_2), a mixture of aluminum oxide (Al_2O_3) and zirconium oxide (ZrO_2), disclosed in

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U.S. Patent No. 3,934,961, and a mixture of lanthanum oxide (La_2O_3) and aluminum oxide (Al_2O_3), disclosed in Japanese Patent Application Laid-Open No. 6-184730, which have been put into use.

[0010] However, when used as optical thin films, the above substances or compounds put into use as being achievable of the intermediate refractive index (about 1.6 to 1.9) have problems respectively as stated below. Thus, any substances or compounds suited as optical thin films having an intermediate refractive index are substantially almost unavailable.

[0011] That is, the silicon monoxide (SiO) has a problem that thin films cause an absorption to result in a decrease of transmittance. The magnesium oxide (MgO) has a problem that it reacts with water or carbon dioxide in the air to change into magnesium hydroxide or magnesium carbonate to cause clouding. The lead fluoride (PbF_2) has a problem of environmental pollution due to lead.

[0012] The mixture of aluminum oxide (Al_2O_3) and zirconium oxide (ZrO_2), though having a good reproducibility of refractive index, has a problem that it may cause a compositional deviation in materials because of a difference in vapor pressure to make it unable to carry out cost-advantageous continuous deposition while replenishing materials. The mixture of lanthanum oxide (La_2O_3) and aluminum oxide (Al_2O_3) has a problem that the lanthanum oxide in the mixture reacts with water in the air to change into lanthanum hydroxide to cause expansion, making sintered evaporation source materials and formed films break down. Their breaking down into powder causes fine particulate matters because of chemicals which may scatter when dissolved, to further cause a problem of compositional deviation in film materials during the deposition.

[0013] As stated above, although various deposition materials are conventionally used as substances or mixtures achievable of the refractive index intermediate between alumina (about 1.65) and zirconia (about 2.0), they have properties not undesirable as deposition materials, causative of compositional deviation or occurrence of absorption during the deposition.

SUMMARY OF THE INVENTION

[0014] A first object of the present invention is to solve the above problems the prior art has had, and provide a material for optical thin films which has a relatively high refractive index and does not cause any compositional deviation to enable continuous deposition when used as a vacuum deposition material, and does not cause any deterioration due to ultraviolet-light irradiation, and also to provide an optical device having superior optical characteristics, comprising an optical thin film formed by coating such a material.

[0015] A second object of the present invention is to provide a material for optical thin films which has a refractive index of about 1.65 to 1.9, does not cause any compositional deviation to enable continuous deposition when used as a vacuum deposition material, and has good quality, and also to provide an optical device having superior optical characteristics, comprising an optical thin film formed by coating such a material.

[0016] To achieve the above objects, the present invention provides an optical-thin-film material comprising a metal oxide containing samarium and titanium.

[0017] The present invention also provides an optical device comprising:

a substrate; and

an optical thin film comprising the above optical-thin-film material, formed on the substrate.

[0018] The present invention also provides an optical device comprising:

a substrate;

a plurality of first optical thin films comprising the above optical-thin-film material, formed on the substrate; and

a plurality of second optical thin films each having a lower refractive index than the first optical thin films and superposed on the substrate alternately with the first optical thin films.

[0019] As another embodiment of the optical-thin-film material, the present invention provides an optical-thin-film material comprising a compound represented by the following chemical formula:



wherein $-1 < x < 1$; and

also provides an optical device comprising such an optical-thin-film material and corresponding to the above two types of optical devices.

[0020] The present invention still also provides a process for producing the above optical-thin-film materials, the process comprising the steps of:

mixing samarium oxide and aluminum oxide; and
sintering, melting and solidification the resultant mixture in vacuum or in the atmosphere.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021]

Fig. 1 is a schematic illustration of an optical system employing anti-reflection films formed of the optical-thin-film material of the present invention.

Fig. 2 is a schematic cross-sectional illustration of an example of layer configuration of an anti-reflection film formed on a lens of the optical system shown in Fig. 1.

Fig. 3 is a schematic cross-sectional illustration of another example of layer configuration of an anti-reflection film formed on a lens of the optical system shown in Fig. 2.

Fig. 4 is a graph showing changes in refractive index and film-compositional proportion in instances where optical-thin-film materials of an Example of the present invention and a Comparative Example were deposited continuously.

Fig. 5A and Fig. 5B are each a graph showing wavelength dispersion of absorptivity in a film deposited on the first time and a film deposited on the 10th time.

Fig. 6 is a graph showing changes in refractive index in instances where optical-thin-film materials of two Example of the present invention, having different molar ratios of samarium and aluminum.

Fig. 7 is a graph showing wavelength dispersion of absorptivity in a film formed by depositing the optical-thin-film material of the present invention in which samarium and aluminum are in a molar ratio of 0.5.

Fig. 8 is a graph showing wavelength dispersion of absorptivity in a film formed by depositing the optical-thin-film material of the present invention in which samarium and aluminum are in a molar ratio of 0.33.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0022] An optical-thin-film material having a relatively high refractive index will be described first, which is a first embodiment of the present invention. This optical-thin-film material comprises a metal oxide containing samarium (Sm) and titanium (Ti) as metallic elements, and preferably a sintered product or fused product composed chiefly of from 10 to 80% by weight of samarium oxide (Sm_2O_3) and the balance of titanium oxide (TiO_2).

[0023] This sintered product is obtained by a production process comprising mixing a powder of samarium oxide and a powder of titanium oxide in a desired compositional proportion as described above, and pressure-molding the resultant mixture into granules or a platelike target, followed by sintering in vacuum or in the atmosphere at a temperature of 1,400°C or above. The pressure-molded product before sintering may be melted at a higher temperature and then solidified to form a fused product.

[0024] Such a sintered product or fused product is melted and evaporated chiefly by means of an electron gun and is formed by deposition as an optical thin film on any intended substrate. The sintered product or fused product is melted chiefly by means of an electron gun, but resistance heating, high-frequency heating, or sputtering may also be used.

[0025] In the optical-thin-film material comprising from 10 to 80% by weight of samarium oxide and the balance of titanium oxide, the compositional proportion of a mixture of the both may be changed to set its refractive index selectively to any desired value within the range of from 1.9 to 2.4. Also, the optical-thin-film material does not scatter during the melting with an electron gun and also does not cause any compositional variations, and hence continuous film formation can be made.

[0026] Needless to say, the optical thin film having a high refractive index, formed using the material according to the first embodiment of the present invention, may superpositively be formed in combination with other optical thin films having various refractive indexes to make up optical multi-layer thin films to obtain various multi-layer thin films having good optical characteristics.

[0027] In the present invention, the substrate on which the optical thin film is formed may include, but not particularly limited to, optical glass such as prisms, filters and so forth, as well as display screens of cathode ray tubes, and lenses of eye-glasses and cameras.

[0028] The optical thin film having a high refractive index, formed using the material according to the first embodiment of the present invention, does not cause any increase in absorptivity even upon irradiation by ultraviolet light, and does not cause any problem even when bonded with an ultraviolet-curable resin.

[0029] Fig. 1 schematically illustrates an optical system employing as an anti-reflection film a film formed of the optical-thin-film material of the present invention. In Fig. 1, reference numerals 1 and 2 each denote a lens. Anti-reflection films are formed on light incident and emergent surfaces of these lenses 1 and 2.

[0030] Fig. 2 schematically cross-sectionally illustrates an example of layer configuration of an anti-reflection film formed on any of the lenses 1 and 2 of the optical system shown in Fig. 1. In Fig. 2, reference numeral 11 denotes a substrate constituting the lens. On the substrate 11, high-refractive-index layers 12₁ and 12₂ and low-refractive-index layers 13₁ and 13₂ are alternately superposed. As materials for the high-refractive-index layers 12₁ and 12₂, the metal oxide containing samarium and titanium, which is the first embodiment of the present invention, is used. As materials for the low-refractive-index layers 13₁ and 13₂, SiO₂ is used. Also, the high-refractive-index layers 12₁ and 12₂ each have a refractive index of 2.17 to near ultraviolet light of 365 nm in wavelength, and the low-refractive-index layers 13₁ and 13₂, a refractive index of 1.45.

[0031] The optical-thin-film material according to the first embodiment of the present invention will be described below in greater detail by giving Examples for deposition materials. The present invention is by no means limited to these Examples.

(Example 1)

[0032] Powder of samarium oxide (Sm₂O₃) and powder of titanium oxide (TiO₂) were mixed in a weight ratio of 69:31 (molar ratio 1:2), and the mixture obtained was pressure-molded into granules, followed by sintering at 1,580°C for 4 hours in the atmosphere to produce a granular deposition material.

[0033] This granular deposition material was set in a depositing hearth of an electron gun (JEBG102, manufactured by Nippon Denshi K.K.) disposed in a vacuum deposition coater (BMC850, manufactured by Shincron CO., LTD.). The inside of the system was evacuated up to 1×10^{-5} Torr. Thereafter, electron beams were applied under pressure condition of 1×10^{-4} Torr as oxygen partial pressure to cause the deposition material to melt and evaporate and to deposit in an optical film thickness of $nd = 125$ nm on a synthetic quartz flat plate having been set in the vacuum vessel and heated to a temperature of about 300°C. During this deposition, the deposition material was seen not to scatter. After the deposition was completed, the synthetic quartz flat plate was taken out. On the thin film formed thereon, its absorption (A) and refractive index (n) were calculated from its transmittance (T) and reflectance (R) determined with a spectrophotometer (Model U-3410, manufactured by Hitachi Ltd.) to make evaluation of the thin film. The absorption (A) was calculated according to the following expression (1), and the refractive index (n) according to the following expression (2).

$$A = 100 - (T + R) \quad (1)$$

$$n = \{n_s \times (1 + R^{1/2}) / (1 - R^{1/2})\}^{1/2} \quad (2)$$

[0034] Where n_s is the index of substrate.

[0035] As a result of this evaluation, the optical thin film according to the present Example had a refractive index (n) of 2.18 at wavelength 487 nm as shown in Table 1, and showed no absorption in the visible region and up to wavelength of 370 nm.

[0036] The synthetic quartz flat plate provided with the optical thin film of the present Example was also irradiated by ultraviolet rays of 360 nm in wavelength and 200 mW/cm² in intensity for 5 seconds by means of an ultraviolet ray irradiator (SUNCURE202-PS, manufactured by AGC), and its absorptivity was measured immediately thereafter to find that the absorptivity was 0.2% or less in the visible region and there was seen no increase.

(Example 2)

[0037] A granular deposition material was produced in the same manner as in Example 1 except that the powder of samarium oxide (Sm₂O₃) and powder of titanium oxide (TiO₂) were mixed in a weight ratio of 54:46 (molar ratio 1:4). The subsequent procedure of Example 1 was repeated to deposit an optical thin film on a synthetic quartz flat plate. Thereafter, the optical thin film was tested similarly to find that the optical thin film had a refractive index (n) of 2.37 as shown in Table 1 and showed no absorption in the visible region and up to wavelength of 370 nm.

[0038] The synthetic quartz flat plate provided with the optical thin film of the present Example was also irradiated by ultraviolet rays in the same manner as in Example 1, and its absorptivity was measured to find that there was seen no increase in absorptivity.

(Example 3)

[0039] A granular deposition material was produced in the same manner as in Example 1 except that the powder of samarium oxide (Sm₂O₃) and powder of titanium oxide (TiO₂) were mixed in a weight ratio of 81:19 (molar ratio 1:1). The subsequent procedure of Example 1 was repeated to deposit an optical thin film on a synthetic quartz flat plate.

Thereafter, the optical thin film was tested similarly to find that the optical thin film had a refractive index (n) of 2.03 as shown in Table 1 and showed no absorption in the visible region and up to wavelength of 370 nm.

[0040] The synthetic quartz flat plate provided with the optical thin film of the present Example was also irradiated by ultraviolet rays in the same manner as in Example 1, and its absorptivity was measured to find that there was seen no increase in absorptivity.

(Example 4)

[0041] The procedure of Example 1 was repeated except that thin films of 125 nm in optical film thickness were continuously deposited ten times without replenishing the granular deposition material. The films formed were compositionally analyzed with a fluorescent X-ray analyzer (RIX-3000, manufactured by Rigaku Denki K.K.), and there was seen no compositional change. Their refractive index (n) was also measured, and similarly there was seen no change.

(Comparative Example 1)

[0042] Powder of lanthanum oxide (La_2O_3) and powder of titanium oxide (TiO_2) were mixed in a weight ratio of 67:33 (molar ratio 1:2), and the mixture obtained was molded into granules, followed by sintering at 1,590°C for 8 hours in vacuum to produce a granular deposition material (the compound represented by the formula $\text{La}_2\text{Ti}_2\text{O}_{7-x}$; $x = 0.3$ to 0.7). This granular deposition material was deposited on a synthetic quartz flat plate in the same manner as in Example 1, which was then irradiated by ultraviolet rays, and its absorptivity was measured immediately thereafter to find that, as shown in Table 1, the absorptivity was seen to increase by 2.4% or more.

(Comparative Example 2)

[0043] The granular deposition material ($\text{Sm}_2\text{Ti}_2\text{O}_7$) produced by mixing powder of samarium oxide (Sm_2O_3) and powder of titanium oxide (TiO_2) in a weight ratio of 69:31 (molar ratio 1:2), followed by molding and sintering, and the granular deposition material ($\text{La}_2\text{Ti}_2\text{O}_{7-x}$; $x = 0.3$ to 0.7) produced by mixing powder of lanthanum oxide (La_2O_3) and powder of titanium oxide (TiO_2) in a weight ratio of 67:33 (molar ratio 1:2) were each weighed out in equal weights (4 g, 5 g and 7 g). These were each melted and evaporated by means of an electron gun, and the time (premelting time) taken until the scattering of the material went down under equal conditions was measured. As a result, the deposition material comprising samarium oxide and titanium oxide according to the present invention caused no scattering of material and also, as shown in Table 2, showed a short melting time. Thus, this is a material preferable as a material for continuous deposition. On the other hand, the deposition material comprising lanthanum oxide and titanium oxide greatly scattered to take a time to melt.

Table 1

Deposition material	Refractive index	* Absorptivity
Samarium oxide:titanium oxide = 69:31 (weight ratio)	2.18	0.2
Samarium oxide:titanium oxide = 54:46 (weight ratio)	2.37	0.3
Samarium oxide:titanium oxide = 81:19 (weight ratio)	2.03	0.2
$\text{La}_2\text{Ti}_2\text{O}_{7-x}$ ($x = 0.3$ to 0.7)	-	2.4

* after ultraviolet-light irradiation

Table 2

Deposition material	Melting time		
	4 g	5 g	7 g
Samarium oxide:titanium oxide = 69:31 (weight ratio)	0'38"	0'52"	1'07"
$\text{La}_2\text{Ti}_2\text{O}_{7-x}$ ($x = 0.3$ to 0.7)	3'39"	5'49"	9'22"

[0044] An optical-thin-film material having an intermediate refractive index of from 1.65 to 1.9 will be described below, which is a second embodiment of the present invention. This optical-thin-film material comprises a metal oxide containing samarium (Sm) and aluminum (Al) as metallic elements. It is produced by mixing samarium oxide (Sm_2O_3) and aluminum oxide (Al_2O_3) in a desired compositional proportion and, in a sense that the film composition is stable, preferably in such a proportion that the samarium oxide is 0.3 or more in molar ratio to the aluminum oxide, followed by sintering, or melting and solidification. This material is compositionally represented by the chemical formula: $\text{Sm}_{1-x}\text{Al}_{1+x}\text{O}_3$ (wherein $-1 < x < 1$).

[0045] A sintered product of this material is obtained by mixing powder of samarium oxide and powder of aluminum oxide in a desired compositional proportion as described above, and press-molding the resultant mixture, followed by sintering in vacuum or in the atmosphere at a temperature of about $1,500^\circ\text{C}$. After sintering, the sintered product obtained is pulverized to produce a granular deposition material of 1 to 3 mm in diameter.

[0046] The sintered product or the like of the deposition material is melted and evaporated chiefly by means of an electron gun and is formed by deposition as an optical thin film on any intended substrate. The sintered product is melted chiefly by means of an electron gun, but resistance heating or high-frequency heating may also be used.

[0047] In the optical-thin-film material according to the second embodiment of the present invention, the compositional proportion of the samarium oxide and aluminum oxide may be changed to set its refractive index to any desired value, which can selectively be set within the range of from 1.65 to 1.9. Also, the compositional proportion in the optical thin film can be stable, and continuous deposition can be carried out while replenishing materials. Also, no remarkable absorption or clouding is seen, and optical thin films free of fine particulate matters which may be caused by scattering of chemicals can be obtained, also making it easy to work and use the products.

[0048] In the second embodiment of the present invention, too, the substrate on which the optical thin film is formed may include, but not particularly limited to, optical glass serving as substrates of prisms, filters and so forth, as well as display screens of cathode ray tubes, and lenses of eye-glasses and cameras.

[0049] Needless to say, the optical thin film having an intermediate refractive index, formed using the material according to the second embodiment of the present invention, may superposingly be formed in combination with other optical thin films having various refractive indexes to make up optical multi-layer thin films to obtain various multi-layer thin films having good optical characteristics.

[0050] Fig. 3 schematically illustrates an example in which the optical-thin-film material according to the second embodiment of the present invention is used in the anti-reflection films formed on the lenses 1 and 2 of the optical system shown in Fig. 1. In Fig. 3, reference numeral 21 denotes a substrate constituting the lens. On the substrate 21, high-refractive-index layers 22_1 , 22_2 and 22_3 and low-refractive-index layers 23_1 , 23_2 and 23_3 are alternately superposed. As materials for the high-refractive-index layers 22_1 , 22_2 and 22_3 , $\text{Sm}_{1-x}\text{Al}_{1+x}\text{O}_3$ (wherein $-1 < x < 1$) is used. As materials for the low-refractive-index layers 23_1 , 23_2 and 23_3 , SiO_2 is used. Also, the high-refractive-index layers 22_1 , 22_2 and 22_3 each have a refractive index of 1.73 to light of 248 nm in wavelength, and the low-refractive-index layers 23_1 , 23_2 and 23_3 , a refractive index of 1.51.

[0051] The optical-thin-film material according to the second embodiment of the present invention will be described below in greater detail by giving Examples. The present invention is by no means limited to these Examples.

(Example 5)

[0052] Powder of samarium oxide (Sm_2O_3) and powder of aluminum oxide (Al_2O_3) were so mixed that the molar ratio of Sm and Al (Sm/Al) was 1, and the mixture obtained was pressure-molded. Thereafter, the molded product obtained was sintered at $1,500^\circ\text{C}$ for about 4 hours in a vacuum of 1×10^{-4} Torr or below, followed by pulverization to produce a granular deposition material of 1 to 3 mm in diameter.

[0053] Next, this granular deposition material was loaded in a depositing hearth of an electron gun disposed in a vacuum deposition coater (BMC850, manufactured by Shincron CO., LTD.). The inside of the reactor was evacuated up to a pressure of 1×10^{-5} Torr. Thereafter, oxygen gas was fed into the reactor at 1×10^{-4} Torr and electron beams with an accelerating voltage of 8 kV and an emission current of 400 mA were applied to heat and melt the deposition material. Thereafter, on a depositing substrate made of glass, having been set in the reactor and heated to a temperature of about 300°C , an optical thin film with an optical film thickness of $\lambda/4$ ($\lambda = 480$ nm) was deposited at a deposition rate of about 10 \AA/second . This deposition was continuously carried out ten times on different substrates.

[0054] On each optical thin film thus formed, the refractive index was calculated from peak values of its spectral characteristics and the samarium concentration (in terms of oxide; % by weight) in the film was measured by fluorescent X-ray analysis to obtain the results shown in Fig. 4. With regard to wavelength dispersion of absorptivity in the film deposited on the first time and the film deposited on the 10th time, results are shown in Figs. 5A and 5B. Also, the optical thin films formed were put to a weathering test in a thermo-hygrostat (60°C , 95%RH, 100 hours), and whether or not any clouding or yellowing occurred was visually examined.

[0055] As a result, the refractive index and the samarium concentration in each film were kept stable as shown in

Fig. 4 (by dotted lines with white circles and black circles, respectively). Also, no absorption was seen as shown in Figs. 5A and 5B. Still also, neither absorption nor clouding was seen after the weathering test.

(Example 6)

[0056] Powder of samarium oxide (Sm_2O_3) and powder of aluminum oxide (Al_2O_3) were so mixed that the molar ratio of Sm and Al (Sm/Al) was 0.5, and the mixture obtained was pressure-molded. Thereafter, the molded product obtained was sintered at $1,500^\circ\text{C}$ for about 4 hours in a vacuum of 1×10^{-4} Torr or below, followed by pulverization to produce a granular deposition material of 1 to 3 mm in diameter.

[0057] Next, using this deposition material, optical thin films were continuously deposited ten times on different substrates in the same manner as in Example 5. On each optical thin film thus formed, the refractive index was calculated from peak values of its spectral characteristics and the wavelength dispersion of absorptivity were measured in the same way. Results obtained are shown in Figs. 6 and 7. Also, the optical thin films formed were put to a weathering test in a thermo-hygrostat (60°C , 95%RH, 100 hours), and whether or not any clouding or yellowing occurred was visually examined.

[0058] As a result, in the present Example, too, the refractive index was kept stable as shown in Fig. 6, and no absorption was seen as shown in Fig. 7. Also, neither absorption nor clouding was seen after the weathering test.

(Example 7)

[0059] Powder of samarium oxide (Sm_2O_3) and powder of aluminum oxide (Al_2O_3) were so mixed that the molar ratio of Sm and Al (Sm/Al) was 0.33, and the mixture obtained was pressure-molded. Thereafter, the molded product obtained was sintered at $1,500^\circ\text{C}$ for about 4 hours in a vacuum of 1×10^{-4} Torr or below, followed by pulverization to produce a granular deposition material of 1 to 3 mm in diameter.

[0060] Next, using this deposition material, optical thin films were continuously deposited ten times on different substrates in the same manner as in Example 5. On each optical thin film thus formed, the refractive index was calculated from peak values of its spectral characteristics and the wavelength dispersion of absorptivity were measured in the same way. Results obtained are shown in Figs. 6 and 8. Also, the optical thin films formed were put to a weathering test in a thermo-hygrostat (60°C , 95%RH, 100 hours), and whether or not any clouding or yellowing occurred was visually examined.

[0061] As a result, in the present Example, too, the refractive index was kept stable as shown in Fig. 6, and no absorption was seen as shown in Fig. 8. Also, neither absorption nor clouding was seen after the weathering test.

(Example 8)

[0062] Powder of samarium oxide (Sm_2O_3) and powder of aluminum oxide (Al_2O_3) were so mixed that the molar ratio of Sm and Al (Sm/Al) was 1, and the mixture obtained was pressure-molded. Thereafter, the molded product obtained was sintered at $1,500^\circ\text{C}$ for about 4 hours in a vacuum of 1×10^{-4} Torr or below, followed by pulverization to produce a granular deposition material of 1 to 3 mm in diameter.

[0063] Using this deposition material, deposition was continuously carried out five times in the same manner as in Example 5. Thereafter, the depositing hearth of the electron gun was replenished with the above deposition material, and the deposition was again continuously carried out five times. On each optical thin film thus formed, the refractive index was calculated from peak values of its spectral characteristics and the samarium concentration (in terms of oxide; % by weight) in the film was measured by fluorescent X-ray analysis.

[0064] As a result, in the present Example, too, the refractive index was kept stable and the samarium concentration in the film was also kept stable.

(Comparative Example 3)

[0065] Powder of lanthanum oxide (La_2O_3) and powder of aluminum oxide (Al_2O_3) were so mixed that the molar ratio of La and Al (La/Al) was 1, and the mixture obtained was pressure-molded. Thereafter, the molded product obtained was sintered at $1,500^\circ\text{C}$ for about 4 hours in a vacuum of 1×10^{-4} Torr or below, followed by pulverization to produce a granular deposition material of 1 to 3 mm in diameter.

[0066] Next, this granular deposition material was loaded in a depositing hearth of the electron gun disposed in the vacuum deposition coater. The inside of the reactor was evacuated up to a pressure of 1×10^{-5} Torr. Thereafter, oxygen gas was fed into the reactor at 1×10^{-4} Torr and electron beams with an accelerating voltage of 8 kV and an emission current of 400 mA were applied to heat and melt the deposition material. Thereafter, on a depositing substrate made of glass, having been set in the reactor and heated to a temperature of about 300°C , an optical thin film with an optical film

thickness of $\lambda/4$ ($\lambda = 480$ nm) was deposited at a deposition rate of about 10 Å/second. This deposition was continuously carried out ten times on different substrates.

[0067] On each optical thin film thus formed, the refractive index was calculated from peak values of its spectral characteristics and the lanthanum concentration (in terms of oxide; % by weight) in the film was measured by fluorescent X-ray analysis to obtain the results shown in Fig. 4.

[0068] In the present Comparative Example, as shown in Fig. 4 (by dotted lines with white triangles and black triangles), the refractive index was unstable for each of the deposition times and the lanthanum concentration in each film showed a tendency of decrease, showing a result unsuited for the formation of optical thin films having stable refractive indexes.

(Comparative Example 4)

[0069] Powder of magnesium oxide (MgO) was pressure-molded. Thereafter, the molded product obtained was sintered at 1,500°C for about 4 hours in the atmosphere, followed by pulverization to produce a granular deposition material of 1 to 3 mm in diameter. Then, using this deposition material, optical thin films were deposited in the same manner as in Example 5. Thereafter, the optical thin films formed were put to a weathering test in a thermo-hygrostat (60°C, 95%RH, 100 hours), and whether or not any clouding or yellowing occurred was visually examined.

[0070] As a result, the optical thin films in the present Comparative Example became cloudy, and were found to be unsuitable for optical purposes.

[0071] An optical-thin-film material comprising a metal oxide containing samarium and titanium, or comprising a compound represented by the following chemical formula:



wherein $-1 < x < 1$ is disclosed. An optical device having an optical thin film formed of such a material is also disclosed. This optical-thin-film material does not cause any compositional deviation to enable continuous deposition when used as a vacuum deposition material, and does not cause any deterioration due to ultraviolet-light irradiation.

Claims

1. An optical-thin-film material comprising a metal oxide containing samarium and titanium.
2. The optical-thin-film material according to claim 1, wherein the metal oxide comprises a sintered product of samarium oxide and titanium oxide.
3. The optical-thin-film material according to claim 1, wherein the metal oxide comprises a fused product of samarium oxide and titanium oxide.
4. The optical-thin-film material according to claim 1, wherein the metal oxide comprises from 10 to 80% by weight of the samarium oxide and the balance of the titanium oxide.
5. The optical-thin-film material according to claim 4, wherein the metal oxide has a refractive index within the range of from 1.9 to 2.4.
6. An optical device comprising:
 - a substrate; and
 - an optical thin film comprising the optical-thin-film material according to any one of claims 1 to 5, formed on the substrate.
7. An optical device comprising:
 - a substrate;
 - a plurality of first optical thin films comprising the optical-thin-film material according to any one of claims 1 to 5, formed on the substrate; and
 - a plurality of second optical thin films each having a lower refractive index than the first optical thin films and superposed on the substrate alternately with the first optical thin films.

8. An optical-thin-film material comprising a compound represented by the following chemical formula:



wherein $-1 < x < 1$.

9. The optical-thin-film material according to claim 8, wherein the compound comprises a sintered product of samarium oxide and aluminum oxide.

10. The optical-thin-film material according to claim 8, wherein the compound comprises a fused product of samarium oxide and aluminum oxide.

11. The optical-thin-film material according to claim 8, wherein the compound has a refractive index within the range of from 1.65 to 1.9.

12. An optical device comprising:

a substrate; and
an optical thin film comprising the optical-thin-film material according to any one of claims 8 to 11, formed on the substrate.

13. An optical device comprising:

a substrate;
a plurality of first optical thin films comprising the optical-thin-film material according to any one of claims 8 to 11, formed on the substrate; and
a plurality of second optical thin films each having a lower refractive index than the first optical thin films and superposed on the substrate alternately with the first optical thin films.

14. A process for producing the optical-thin-film material according to any one of claims 8 to 11, the process comprising the steps of:

mixing samarium oxide and aluminum oxide; and
sintering or melting and solidified the resultant mixture in vacuum or in the atmosphere.

15. The process according to claim 13, wherein in the mixing step the samarium oxide and the aluminum oxide are so mixed that the molar ratio of samarium to aluminum is 0.3 or more.

FIG. 1

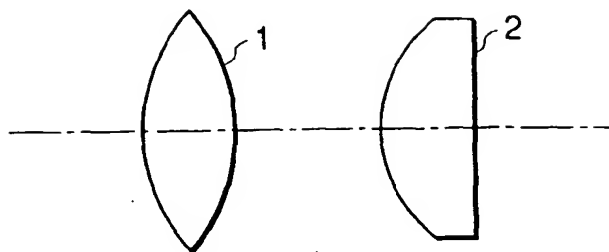


FIG. 2

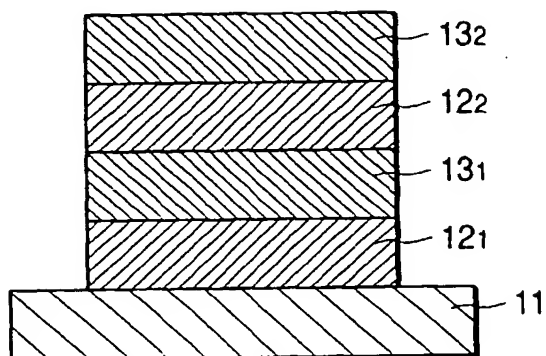


FIG. 3

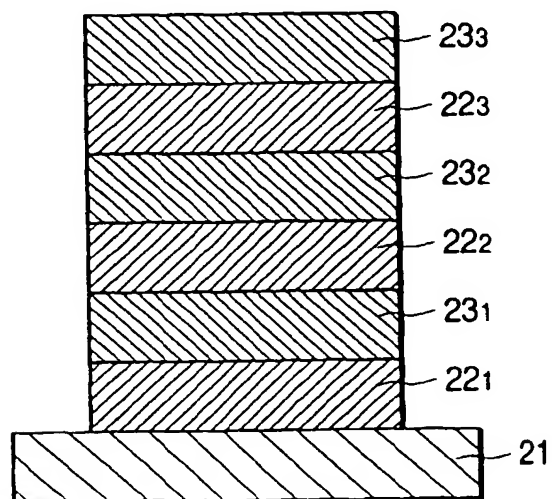


FIG. 4

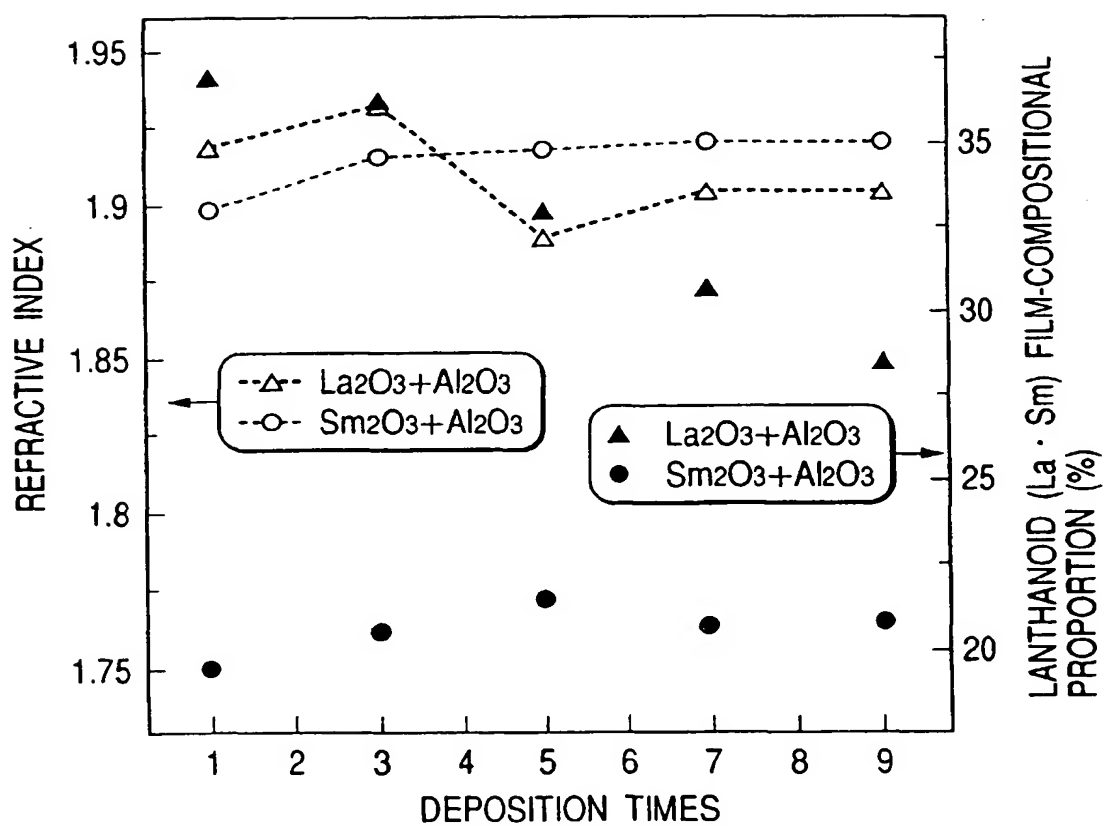


FIG. 5A

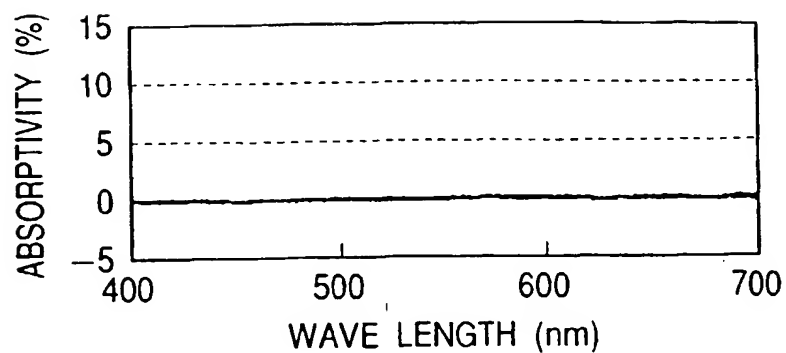


FIG. 5B

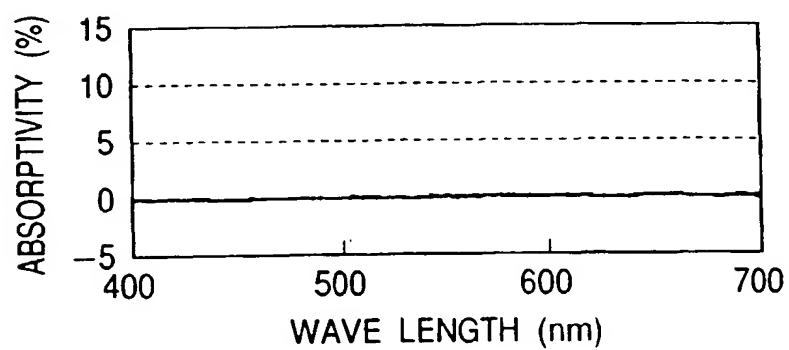


FIG. 6

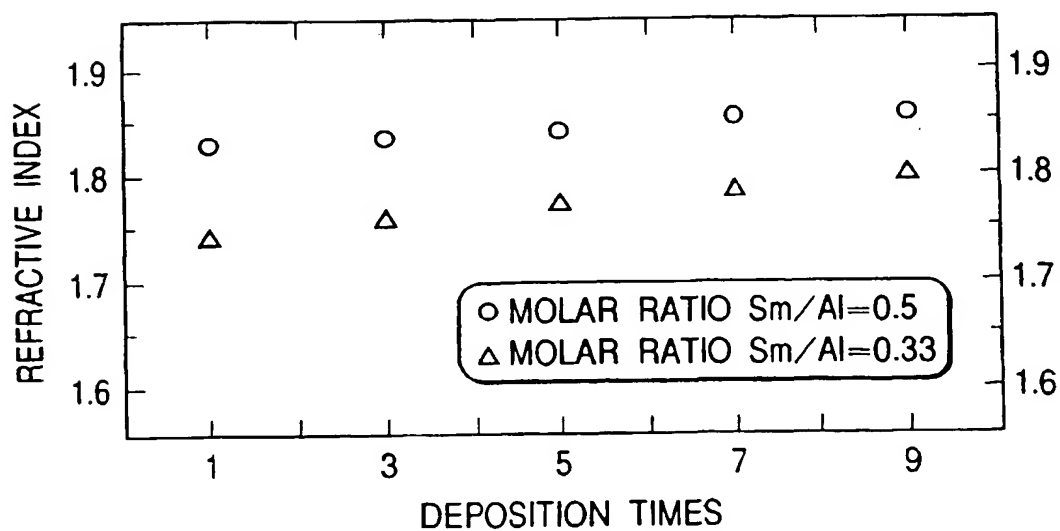


FIG. 7

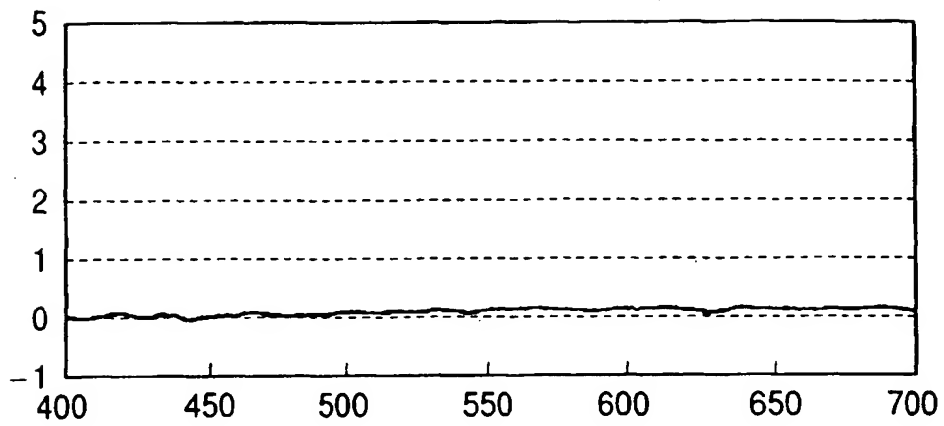
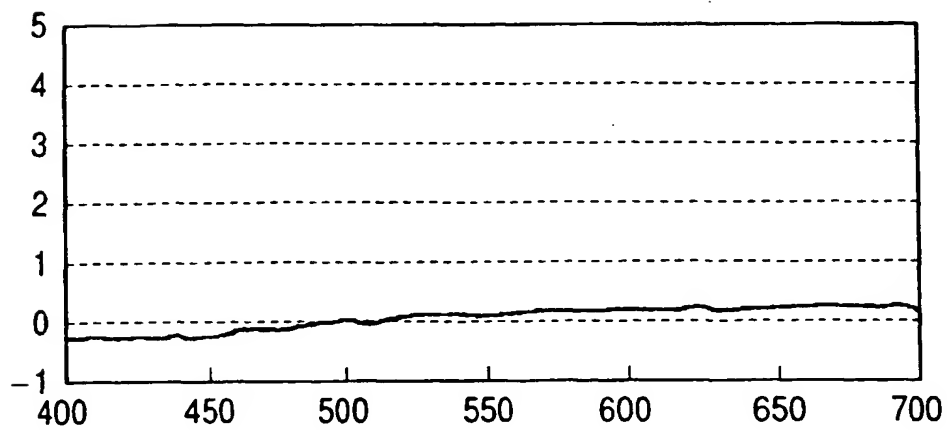


FIG. 8





European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 99 12 4470

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
P,X	US 5 989 626 A (COOMBS PAUL G ET AL) 23 November 1999 (1999-11-23)	1-3	G02B1/11 C03C17/34 C04B35/50
A	* claims 1,3,10-15 *	4,5	
D,A	US 5 340 607 A (ALBRECHT DETLEF ET AL) 23 August 1994 (1994-08-23) * column 2, line 43 - column 4, line 52; examples 1-3 *	1-7	
D,A	US 5 415 946 A (FRIZ MARTIN) 16 May 1995 (1995-05-16) * column 2, line 30 - column 4, line 2; examples 1-3 *	8-15	
A	US 4 927 239 A (MELZIG MANFRED ET AL) 22 May 1990 (1990-05-22) * column 1, line 65 - column 4, line 14; claim 1 *	1-15	
A	US 4 173 778 A (SMALL EDWARD A JR ET AL) 6 November 1979 (1979-11-06) * column 3, line 48 - column 4, line 3 * * column 6, line 21 - line 45; figure 8 *	1-7	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.7) G02B C03C C04B
Place of search THE HAGUE		Date of completion of the search 17 March 2000	Examiner THEOPISTOU, P
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 12 4470

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

17-03-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5989626 A	23-11-1999	US 5641719 A	24-06-1997
		EP 0828696 A	18-03-1998
		JP 11504987 T	11-05-1999
		WO 9635650 A	14-11-1996
US 5340607 A	23-08-1994	DE 4208811 A	23-09-1993
		AT 144842 T	15-11-1996
		CA 2091862 A	20-09-1993
		CN 1076527 A,B	22-09-1993
		DE 59304329 D	05-12-1996
		EP 0561289 A	22-09-1993
		ES 2094398 T	16-01-1997
		HU 66802 A,B	28-12-1994
		JP 2720959 B	04-03-1998
		JP 6235803 A	23-08-1994
US 5415946 A	16-05-1995	DE 4219817 A	23-12-1993
		AT 138420 T	15-06-1996
		CA 2098447 A	18-12-1993
		CN 1083543 A,B	09-03-1994
		CZ 9301120 A	17-08-1994
		DE 59302657 D	27-06-1996
		EP 0574785 A	22-12-1993
		HU 67512 A	28-04-1995
		JP 6184730 A	05-07-1994
		SK 57593 A	12-01-1994
US 4927239 A	22-05-1990	DE 3332872 A	04-04-1985
		AT 59236 T	15-01-1991
		AU 2832689 A	04-05-1989
		AU 3430784 A	11-04-1985
		WO 8501361 A	28-03-1985
		EP 0140096 A	08-05-1985
		EP 0155307 A	25-09-1985
US 4173778 A	06-11-1979	JP 60502173 T	12-12-1985
		NONE	